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## PHASE STABILIZATION OF AMMONIUM NITRATE

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### ABSTRACT

Ammonium nitrate (AN) as an ingredient for solid propellants has problems caused by a large volume phase change in normal operational temperature range, difficulty in keeping dry at relative humidities above 30%, 91 F phase change making smaller AN particles causing propellant grain growth during temperature cycling, and caking behavior that creates a need for processing into propellant relatively soon after grinding to retain small particle sizes. Interference of propellant cure using isocyanate curatives commonly occurs due to moisture content in the AN. AN phase stabilization is typically accomplished by introducing another substance into the ammonium nitrate crystal structure. Salts containing ions larger or smaller than either ammonium or nitrate ions have been used. Since the U.S. military has decided not to use nickel or copper phase stabilizing agents, our laboratory has been looking for new materials for phase stabilizing ammonium nitrate for use in solid propellants. Use of N,N,N',N'-tetramethyl hexane-1,6-diamine appears to solve many AN problems. That is, elimination of phase changes, elimination of propellant grain growth during temperature cycling, lack of moisture for cure interference, and lack of caking in 50% relative humidity environments. How AN can be transformed into a well behaved oxidizer ingredient will be discussed.

### DISCUSSION

Ammonium nitrate (AN) preparations, even phase stabilized ANs, often exhibit a number of problems such as:

- (a) Absorption of moisture from the air at relative humidities of 30% or more.
- (b) Volume changes associated with phase transformations at temperatures within normal tactical missile operating ranges. The moisture induced phase change near 32 Centigrade or above depending on moisture content and heating rate is especially distressing since AN crystals fragment into smaller and smaller particles when temperature cycling up and down through the phase change with void space production (1). A significant aspect of AN phase change from phase IV to phase III and return is that the smaller crystals produced by the process are oriented at different angles to each other. This results in the creation of voids in spaces originally occupied by a larger AN particle. Some AN oxidized solid propellants have grown up to 50% in volume when temperature cycled 100 times through phase IV to phase III and return to phase IV.
- (c) AN particles agglomerate over time either promoted by small amounts of moisture or elevated temperature such as 60 C in a drying oven (1). With adequate time a nearly solid mass will be produced if anticaking measures are not employed.
- (d) AN particle sizes are often unstable and grow in size. This process occurs slowly when dry and cool and more rapidly with small amounts of moisture or elevated temperature storage, such as, 60 C. Zinc oxide phase stabilized AN has been observed to grow from 30 microns to 380 microns in less than one week at ambient temperature.
- (e) Low strength AN adhesive bonds to solid propellant binders that yield soft propellants as compared to use, for example, of ammonium perchlorate as oxidizer.

Accommodations for these problems made by the propellant formulator have been careful drying, process facility relative humidity control to less than 30%, reduced solids loadings to allow propellant castability with monomodal or nonoptimum oxidizer particle distributions, use of fine powder additives to minimize caking traits (1), and employment of formulation tactics that enhance propellant strength and rupture elongation.

Successful use of AN in solid propellants faces many obstacles driven by the natural migratory, absorptive, adhesive, and crystal phase traits of AN. If phase problems were solved, problems of weak particle bonding to propellant binders could still remain and particle size growth with aging could present changing propellant physical strength and rupture elongation characteristics. For these reasons a search for a suitable surface coating for AN particles might produce dividends for solid propellant physical characteristics and make processing high solids loading, AN oxidized solid propellants easier. With these thoughts in mind treatment of AN by amines to produce ammonia and amine nitrate coatings were considered since they could be easy to apply and an amine with lower vapor pressure than ammonia might be able to attain complete surface coverage. However, an amine coating material would have to give improved properties over amine coatings already used commercially (2). While some particle size stability can often be observed by commercially available amine coated AN, they do not give strong propellant binder adhesion or great reduction in moisture absorptivity. A ditertiary amine seemed attractive since two ionic attachment points should yield a nonmigrating salt due to difficulty of having simultaneous dissociation of two ionic structures, tertiary amine salts are higher melting than monosubstituted amine salts, and tertiary amine nitrates are usually less water soluble (less moisture sensitive) than corresponding primary amine nitrates (3). High melting point in the amine nitrate coating material was desirable because low melting eutectic compositions with AN might be unlikely. When AN was treated with an excess of dimethyl benzyl amine, complete ammonia replacement occurred because benzyl amine nitrate and ammonium nitrate readily form a liquid composition so that surface passivation is not possible. In searching through chemical catalogs N,N,N'-tetramethyl-1,6-hexane diamine was available. This seemed a suitable candidate since it had adequate separation between amine functions so that formation of a salt structure with one amine group would not seriously reduce the basicity of the second amine group, and its boiling point, 209 C, indicated appreciable vapor pressure that would allow mobility for treatment of the entire surface of AN particles.

First coatings of AN particles with tetramethyl hexane diamine were accomplished by bubbling nitrogen through the diamine and carrying the vapor through a bed of AN particles supported by a glass filter element. The AN particles had been carefully dried and screened providing an initial free flowing powder. Ammonia evolution was tracked by a Nicolet, Impact 400, Fourier transform spectrometer. When ammonia evolution became undetectable, the coated AN was found to have increased in weight by 1.03%. This was a quite tedious process since vapor pressure of the tetramethyl hexamine was low and the rate of mass transport was slow. Since the amount of tetramethyl hexane diamine needed to halt the ammonia replacement process was fairly large, the layer of tetramethyl hexane diamine dinitrate salt was much thicker than a unimolecular layer. This indicated that some migration of material at the particle surfaces occurred during the diamine treatment of AN.

As a test for the effectiveness of the tetramethyl hexane diamine dinitrate salt coating, samples of the coated AN were subjected to 50% and 90% relative humidities in glass desiccator jars. After exposure to 50% relative humidity for more than sixteen months, the white, hexane diamine coated, AN powder remained free flowing and had not changed in appearance. Deliquescence within an hour was observed with 90% relative humidity condition. Therefore, considerable moisture resistance had been imparted to the AN by the tetramethyl hexane diamine coating since uncoated AN agglomerated into a single mass at 50% relative humidity within four hours. At some point between 50 and 90% relative humidity moisture absorption by the coated particles will begin.

Differential scanning calorimeter (DSC) scan of the tetramethyl hexane diamine coated AN provided a surprise. The typical AN 52 C (Centigrade) phase IV to phase II crystal transition was moved to about 71 C. See Figure 1. After some thought, this behavior with AN crystals seemed to be not so strange. Activation energies for ionic position shifts during phase transitions are likely to be much larger for ions positioned within an ionic matrix than ions positioned at a crystal edge or face. Thus, AN crystal phase changes should most readily initiate on crystal surfaces and migrate across the crystal as phase transition proceeds. If surface initiation is the mechanism for phase transition, installing an outer shell of nonphase transitioning, high melting tetramethyl hexane diamine nitrate salt should provide lattice restraining forces on the most easily moved ions of the AN crystals. As a result, the temperature required for a phase transition should increase until growing thermal agitation provides adequate activation energy

allowing the phase transition to proceed. AN phase transitions have low enthalpy (heat) quantities involved. That is, change in enthalpy with the AN phase transitions are in the range of less than one kilocalorie per mole, e.g., V to IV – 0.13, IV to III – 0.40, III to II – 0.33, and II to I – 0.98 (4,5). Total lattice energy for AN is about 178 kcal/mole (6). Even with some spaced out ionic attachment points for the surface attached tetramethyl hexane diammonium salt its lattice energy contribution to AN crystal surface structure might amount to 50 kcal/mole or more. Lattice energy for the tetramethyl hexane diammonium salt on the surface seems likely to be capable of at least impeding if not overpowering AN phase transitions energies.

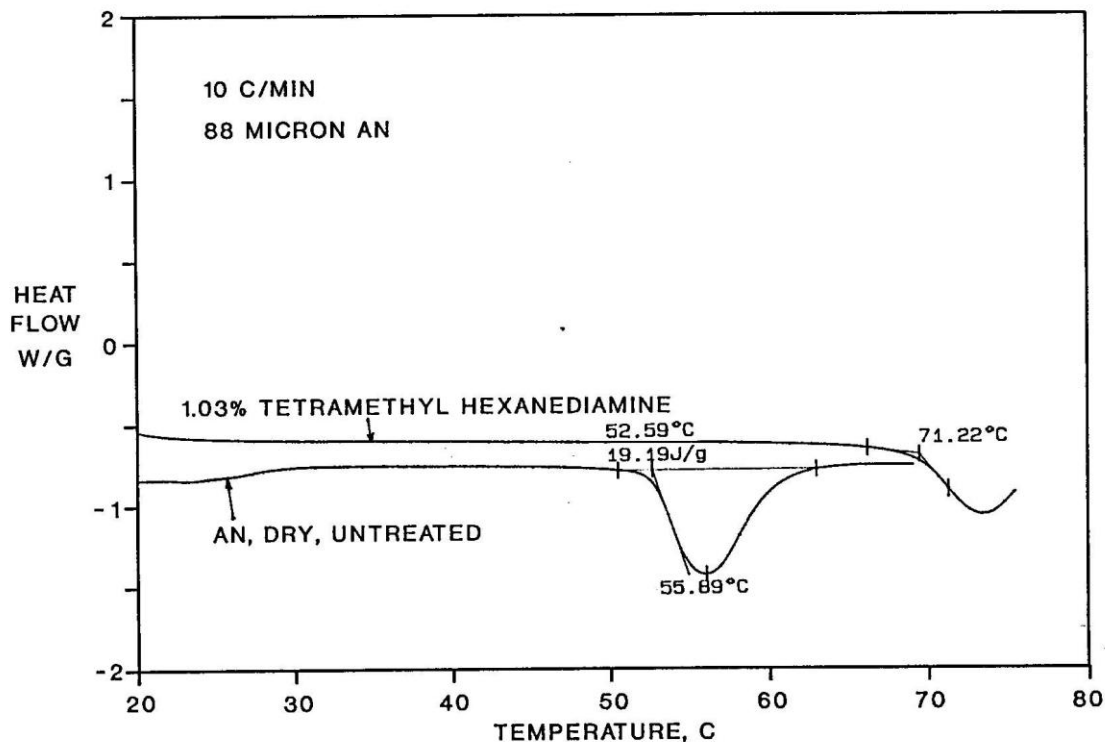


Figure 1. AN and Room Temperature Coated AN Thermogram Comparison. Upper Curve is for AN That Gained 1.03% by Weight When Treated with Tetramethyl Hexane Diamine. Lower Curve is for Untreated AN.

A, perhaps, more interesting coating method was to coat AN at a temperature above 53 C where phase II is stable. AN's phase II is stable from about 53 to 84.2 C (183.6 F), a temperature above the operational 74 C (165 F.) upper temperature limit requirement often observed for tactical missiles. Once coated, would the ionic shell coating restraints on AN ion structure movement freeze the AN crystal phase so that little inclination would be available for making lower temperature phase transitions down to low temperatures? A favorable aspect would be that as AN was cooled thermal agitation energies for activating crystal transitions would diminish. Elimination of all AN phase changes in the tactical missile operational temperature range sounded attractive and a limited amount of experimental work has been carried out.

An elevated temperature coating experiment was conducted in an insulated container where the tetramethyl hexane diamine, AN bed, and nitrogen gas transfer lines were maintained about 53 C. during the vapor transfer and ammonia replacement coating process. After the vapor transfer coating process was completed, a DSC scan was conducted at 10 degrees C per minute. See Figure 2. Although a very small ripple was observed in the DSC scan above 60 C, no clear indications of a phase change was observed. Unfortunately, this work has not been investigated further.

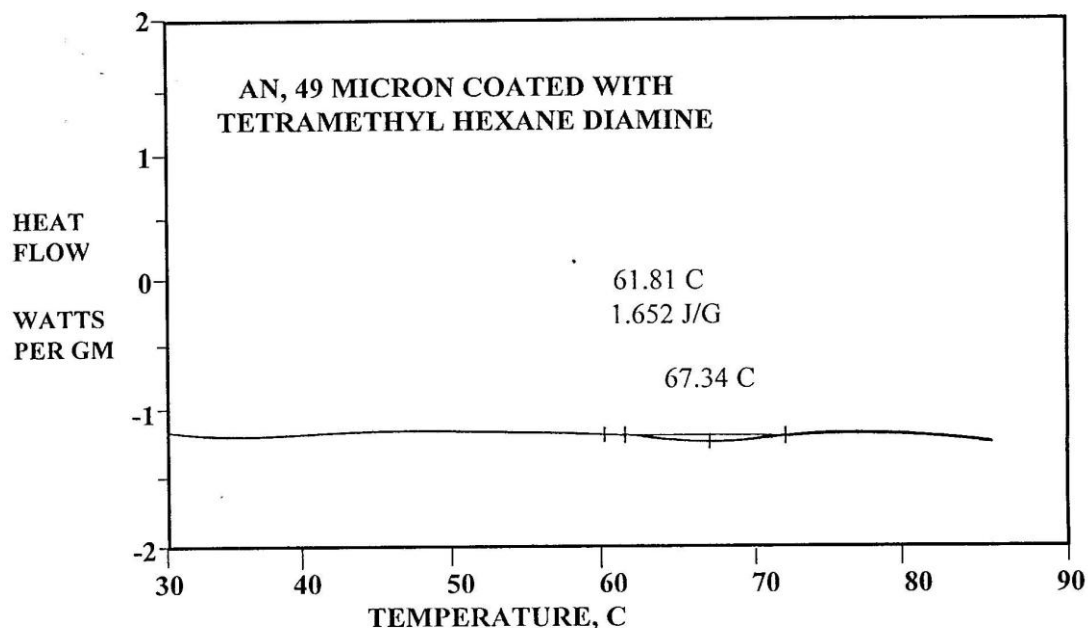


Figure 2. DSC Scan of 53 C Tetramethyl Hexane Diamine Coated AN at 10 C per Minute Almost No Indications of Phase Transitions Are Present. The Very Small Depression at 67 C May Be Due to Slight AN Phase IV Contamination.

#### SUMMARY

Investigation has been conducted looking at behavior of AN powder treated with vapors of tetramethyl hexane diamine at about 20 C. The best hexane diamine treated AN powder seemed highly suitable for use in processing AN oxidized solid propellants. Use of tetramethyl hexane diamine treated AN appears capable of long term age life and capable of tolerating at least 50% relative humidity environments during extended storage periods.

Ammonia was produced by formation of tertiary amine salt coating on the AN particles. Ammonia evolution ceased after adequate exposure to the difunctional tertiary amine vapors. Typical weight increase for a treated AN sample was about one percent. In one case weight increase was 1.03%. Phase change from phase IV to II shifted from 52 to about 71 C. Relative large increase in phase change temperature indicated that AN crystal change was initiated exclusively on crystal surfaces rather than internally. AN phase III is promoted by small amounts of moisture.

Absence of 52 C phase change for the elevated temperature coated AN attested to completeness of AN particle coating. Elevated temperature coated AN particles did not exhibit caking activity over a sixteen month period in a controlled 50% relative humidity environment. Free pouring powder for the coated AN over long term at 50% humidity demonstrated that the tetramethyl hexane diamine coating process on AN totally eliminated AN phase III. This result is notable since the AN IV to III phase change is responsible for propellant grain growth when AN oxidized solid propellants containing a small amount of moisture are repeatedly temperature cycled through the 32 C phase change temperature. Lack of particle caking or intrusion of moisture to internal AN might be expected since normal, low level acid-base dissociation and recombination processes with the diamine salt would always keep at least one end of the tetramethyl hexane diamine ionically fixed in place. At 90% relative humidity, coated AN powder deliquesced, demonstrating that moisture resistance of the coated AN had its limits.

AN lattice energy is about 178 kcal/mole. Phase change energies for AN are less than 1 kilocalorie per mole. The large disparity between lattice energy and phase change energies indicated that even limited lattice energy produced by tertiary amine salt overlaid on AN crystal surfaces might readily overpower propensity for phase changes. Treatment of AN with tetramethyl hexane diamine at 53 C where the AN was exclusively in the form of phase II resulted in a material that exhibited miniscule phase change behavior in the temperature range of 25 to 80 C.

## ACKNOWLEDGEMENT

Louis A. Dee died of intestinal cancer March 20, 2008 in Las Cruces, NM. He was joy to work with and was respected by all who knew him. He was an outstanding, innovative, primarily analytical chemist. His chemical efforts were 37 years at the Air Force Rocket Propulsion Laboratory, Edwards AFB and 8 years at the NASA, White Sands Facility.

A major part of Lou's analytical chemistry research involved creating and correcting analytical analyses provided in Military Standards for fuels, oxidizers, gases, and lubricants determining their suitability for use by our Military Forces. An outgrowth of his rocket fuel analyses was to measure minute amounts of such materials in air for determining environmental safety near propellant tanks and operational equipment. Work described in this presentation was accomplished in 1995 just before Lou moved to New Mexico to work at the NASA, White Sands Facility.

## REFERENCES:

1. "Phase Stabilized Ammonium Nitrate and Method of Making Same," WO 1994017015 19940804.
2. Ammonium Nitrate: A Promising Rocket Propellant Oxidizer," Journal of Hazardous Materials, V 67, p. 253-281, June 1999.
3. Handbook of Chemistry and Physics, 64<sup>th</sup> Edition, 1983-1984.
4. <http://zhurnal.ape.relarn.zu/articles/2007/159.pdf> (Russian)
5. "The Heat Capacity of Ammonium Nitrate from 15 to 315 °K,": C. C. Stephenson, D. R. Benta, and D. A. Stevenson, J. Chem. Phys., V 77, p. 2161-2164, 1955.
6. "Classical and Quantum Mechanical Studies of Crystalline Ammonium Nitrate," Dan C. Sorescu† and Donald L. Thompson, J. Phys. Chem. A, V 105, p. 720-733, 2001.

# **PHASE STABILIZATION OF AMMONIUM NITRATE**

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and  
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# **AN Usage Inhibited by Poor Physical Traits**

**AN volume change near 32 C, +3.7%, phase IV to III**

**III to IV cycling crystal fragmentation causes propellant grain growth**

**Phase III eliminated by scrupulous drying**

**Process propellant at relative humidity <30 %**

**Rapid caking provides short shelf life after grinding**



# AN PHASES vs. TEMPERATURE (WET)

Phase	Temp., C	State	Vol. Chg, <sup>1</sup> , %	$\Delta E$ , kcal/m
I	125 to 169	cubic	+2.3	-
II	84 to 125	tetragonal	-1.7	0.98
III	32 to 84	$\alpha$ -rhombic	+3.7	0.33
IV	-17 to 32	$\beta$ -rhombic	+2.8	0.40
V	-17 to -273	tetragonal	0.01	0.13

<sup>1</sup> Journal of Hazardous Materials, V67, p.253-281, June 1999.

# **AN PHASES vs. TEMPERATURE (DRY)**

<b>Phases</b>	<b>Temp., C</b>	<b>State</b>	<b>Vol. Chg,<sup>1</sup>, %</b>	<b>ΔE, kcal/m</b>
<b>I</b>	<b>125 to 160</b>	<b>cubic</b>	<b>2.3</b>	<b>-</b>
<b>II</b>	<b>52 to 125</b>	<b>tetragonal</b>	<b>2.0</b>	<b>0.66</b>
<b>IV</b>	<b>-17 to 32</b>	<b>β-rhombic</b>	<b>2.8</b>	<b>0.40</b>
<b>V</b>	<b>-17 to -273</b>	<b>tetragonal</b>	<b>-</b>	<b>0.13</b>

**1 Journal of Hazardous Materials, V67, p.253-281, June 1999.**

# **AN CRYSTAL TRAITS**

**Caking behavior indicates that AN moves**

- Internal voids should be self healing  
(AN abhors a void)**

**Most mobile ions are at surface**

**Phase changes should start at crystal surfaces**

# **AN CRYSTAL IONIC COATING**

**AN lattice energy is about 178 kcal/mole**

**Phase change enthalpys are less than 1.0 kcal/mole**

**Ionic coating on AN crystal surface might provide lattice energy greater than phase change enthalpys**

# **AN IONIC COATING QUESTIONS**

**Can ionic coating on AN crystal inhibit phase changes**

**Can ionic coating coverage be complete?**

**Can ionic coating be immobilized?**

**Can moisture sensitivity be reduced?**

# **DESIRED COATING MATERIAL FOR AN**

**Organic amine more basic than  $\text{NH}_3$  and/or lower vapor pressure**

**Melting points increase and water solubility decreases for series of amine salt compounds, e.g.,**

**$\text{NH}_4\text{NO}_3$ ,  $\text{CH}_3\text{NH}_3\text{NO}_3$ ,  $(\text{CH}_3)_2\text{NH}_2\text{NO}_3$ ,  $(\text{CH}_3)_3\text{NHNO}_3$**

**- Tertiary amine salt will minimize water absorption**

**Diamine material with about equal group basicity could give ionic coating that will not shift over time**

# **SELECTED AN COATING MATERIAL**

**N,N,N',N'-tetramethyl-1,6-hexane diamine**



**Tertiary amine, difunctional, ~ equal basicity, low vapor pressure, could cover every available surface site**

# **AN COATING PROCESS**

**Thoroughly dry AN**

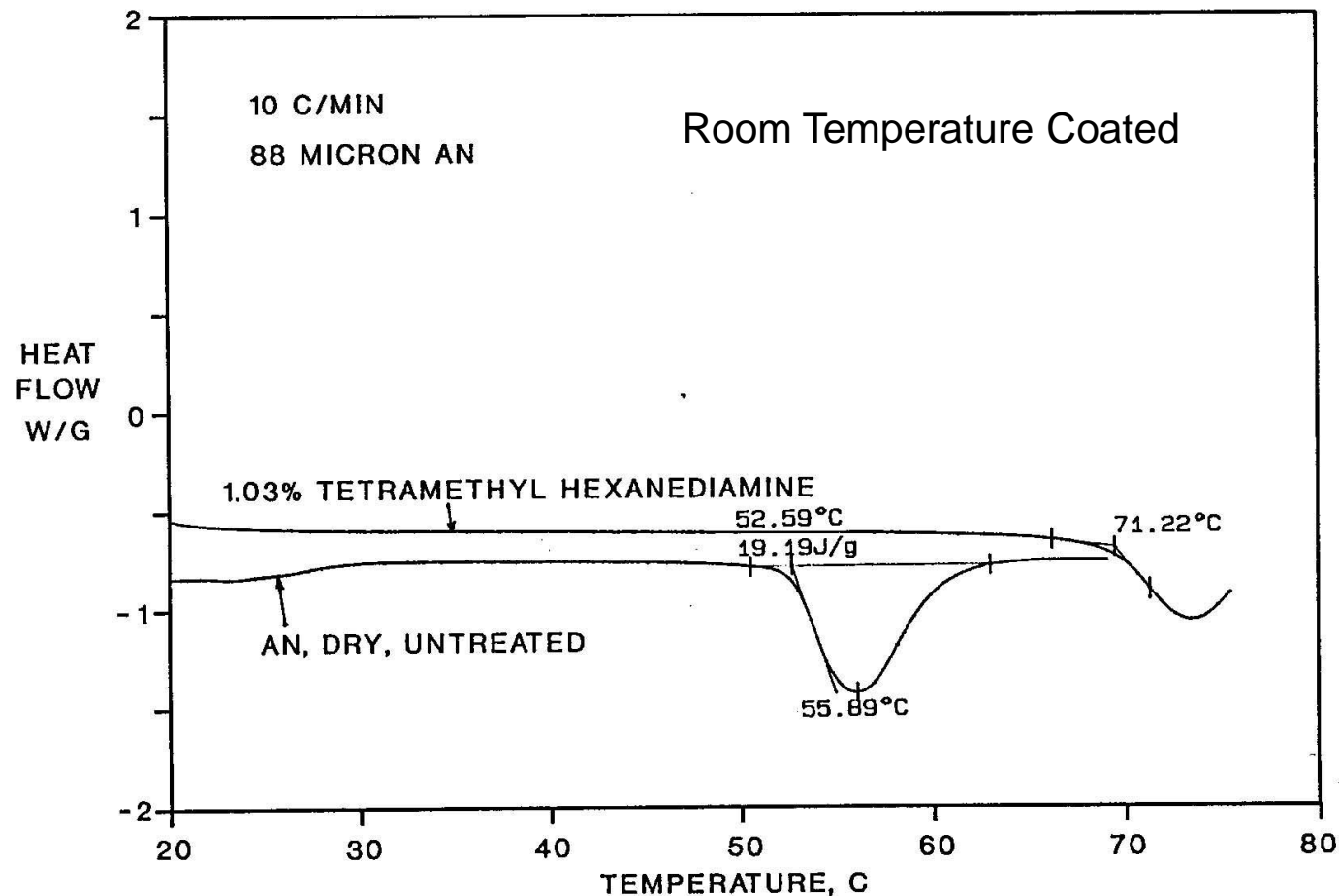
**Grind AN to desired particle size**

**Expose AN to excess tetramethyl hexane diamine vapor**  
**- 1<sup>st</sup> trial at ~20 C, 2<sup>nd</sup> trial at 53 C**

**Remove NH<sub>3</sub> and excess tetramethyl hexane diamine**

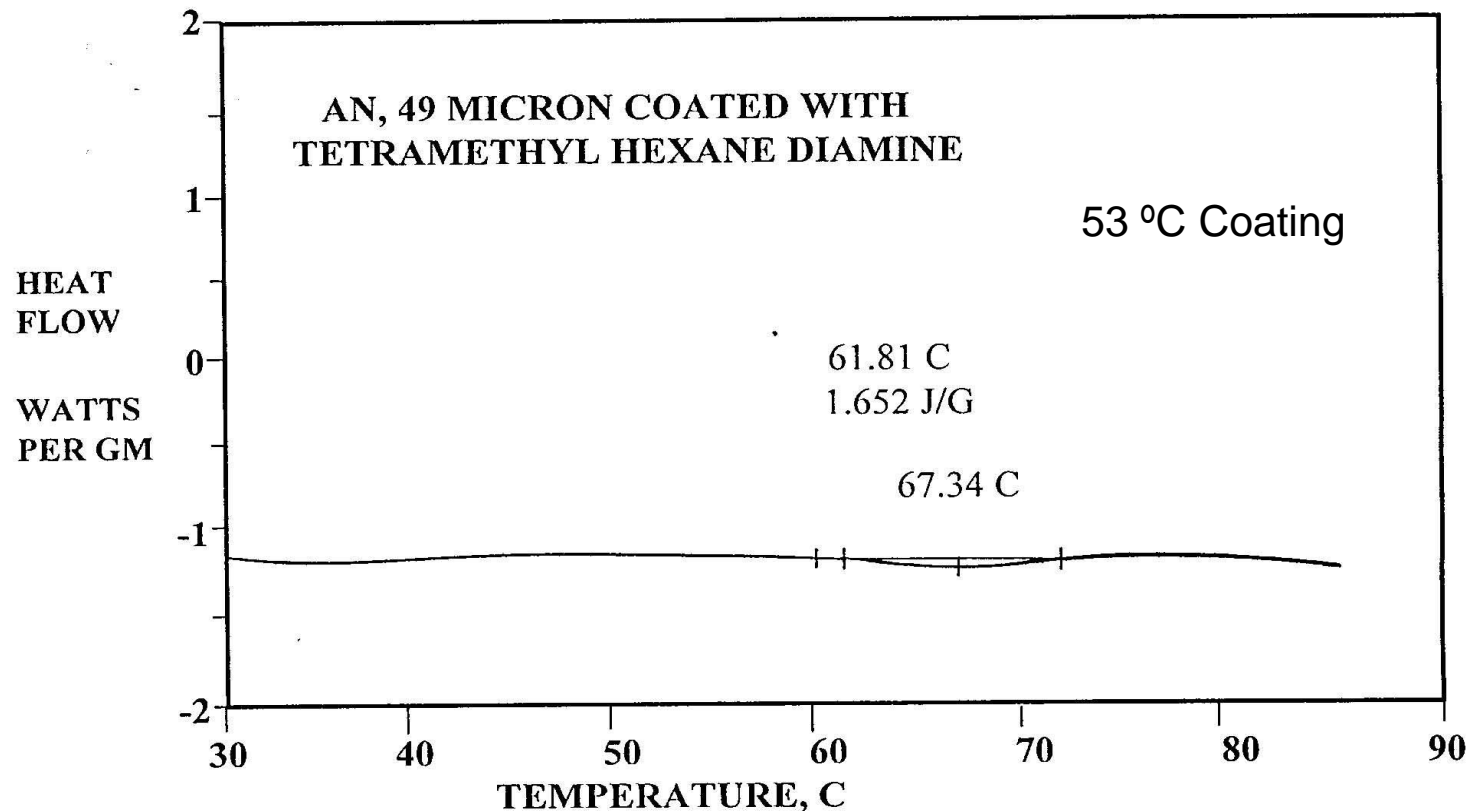


# COATED AN TRAITS



**AN and Room Temperature Coated AN Thermogram Comparison. Upper Curve is for AN That Gained 1.03% by Weight When Treated with Tetramethyl Hexane Diamine. Lower Curve is for Untreated AN.**

# COATED AN TRAITS



**DSC Scan of 53 C Tetramethyl Hexane Diamine Coated AN at 10 C per Minute. Almost No Indications of Phase Transitions Are Present. Small Depression at 67 C May Be Due to Slight AN Phase IV Contamination.**

# **EXTERNAL COATED AN SUMMARY**

**Coating of AN particles with tetramethyl hexane diamine seemed to solve propellant formulation problems**

- No phase changes at normal temperatures**
- No caking**
- Unaffected by 50% relative humidity**

**Has not been put into solid propellant**